Glass and Ceramics, Vol. 70, Nos. 3 – 4, July, 2013 (Russian Original, Nos. 3 – 4, March – April, 2013)

COATINGS

UDC 666.295.1

LOW-MELTING NON-FRIT GLAZES FOR CONSTRUCTION AND ARTISTIC CERAMICS

N. F. Zhernovaya,[1] Yu. V. Burchakova,[1] F. E. Zhernovoi,[1, 2] and E. V. Miroshnikov[1]

Translated from *Steklo i Keramika*, No. 3, pp. 33 – 36, March, 2013.

Low-melting non-frit glazes with firing temperature 950 – 1000°C were obtained in the system datolite–perlite–cullet. The conditions under which high-quality coatings are formed were determined: pre-firing datolite and perlite, $B_2O_3/Al_2O_3 > 2.5$ in the glaze and slip ultradispersity.

Key words: glaze, low-alkali borosilicate glass, batch, wet-milling, activation, melting, efficiency.

One direction of adopting safe energy-conserving technologies in the production of ceramics is to develop and use non-frit (raw) glazes with low firing temperature [1 – 3].

The known non-frit glazes are characterized by high coating formation temperatures (1150 – 1200°C) and are used mainly for decorating porcelain and faience articles and technical ceramics.

During firing of raw glaze diverse physical-chemical processes occur directly on the surface of the ceramic body: decomposition of the raw material, polymorphic transformations, melting and crystallization of phases, glass formation and others. In this connection, the formation process and coating quality largely depend on the material and chemical compositions of the glaze, the fineness of raw-materials grinding and the correctness of the firing regime.

The following materials were used to make low-melting non-frit glazes:

– datolite concentrate (GOST 16108–80) — powder with light-cream color, 78 – 85% of which consists of the mineral datolite $2CaO \cdot B_2O_3 \cdot 2SiO_2 \cdot H_2O$ ($CaBSiO_4(OH)$); the Mohs hardness of datolite is 5 – 5.5; the true density is 2900 – 3000 kg/m^3; datolite concentrate is fire-, explosion-proof and nontoxic; chemical composition of the datolite concentrate (%):[3] 35.5 SiO_2, 18.3 B_2O_3, 0.7 Al_2O_3, 34.5 CaO, 0.2 MgO, 0.2 Na_2O, 2.18 Fe_2O_3 and 5.6 H_2O;

– perlite from the Mukhor-Talinskoe perlite-zeolite deposit (Buryatiya) is a type of volcanic hydrated glass and is characterized by relatively constant chemical composition (%): 70.4 SiO_2, 14.7 Al_2O_3, 0.8 CaO, 0.3 MgO, 3.4 Na_2O, 3.9 K_2O, 0.8 Fe_2O_3 and 5.7 H_2O;

– cullet of NS-3 medical glass (%): 72.8 SiO_2, 6.0 B_2O_3, 4.5 Al_2O_3, 6.8 CaO, 8.1 Na_2O, 1.7 K_2O and ≤ 0.1 Fe_2O_3.

The material composition of the raw experimental glazes (10 compositions) is represented by a concentration triangle where datolite (60%), perlite (40%) and cullet (60%) are the vertices and separation lines are drawn every 10% (Fig. 1). Thus, in the experimental raw glazes the datolite and cullet contents varied from 60 to 30% and perlite from 40 to 10%.

During firing, the batches of non-frit glazes form low-alkali calcium-boro-silicate glassy coatings on ceramic (Table 1). For this reason, the known position of the glass-making state was used to make a preliminary assessment of the batches. The calculations showed that the aluminum and boron cations in the experimental compositions have tetrahedral coordination, and they are integrated in the form of the corresponding cation-oxygen tetrahedra $[AlO_4]^{5-}$ and $[BO_4]^{5-}$ into the structural network, increasing the stability of the glassy state. The connectedness factor Y of the cation-oxygen network (according to N. N. Ermolenko's version [4]) of glaze glasses varies from 3.2 to 3.5, which corresponds to the formation of a layered-framework structure. A. A. Appen's method [5] was used to calculate the properties of glazes: density ρ, CLTE α, index of refraction n and elastic modulus E (Table 1).

It can be assumed a priori that the CLTE for glazes matching well that of the ceramic base ($\alpha = 65 \times 10^{-7}\ K^{-1}$) as well as their high strength will secure the integrity of the coatings and prevent cracks and chipping, while the high

[1] V. G. Shukhov Belgorod State Technological University, Belgorod, Russia.

[2] E-mail: fedor.zhernovoy@gmail.com.

[3] Here and below, content by weight, wt.%.

TABLE 1. Chemical Compositions and Properties of Non-Frit Glazes

Composition	Oxide content, wt.%						Properties			
	SiO_2	B_2O_3	Al_2O_3	CaO	MgO	Na_2O	ρ, kg/m^3	$\alpha \times 10^7$, K^{-1}	n_D	E, GPa
1	50.18	12.78	3.24	22.82	0.15	3.79	2662	68.3	1.564	91.1
2	53.67	10.95	4.64	19.45	0.16	4.50	2616	67.8	1.553	87.9
3	53.91	11.55	3.62	20.05	0.13	4.75	2625	69.1	1.555	88.4
4	57.16	9.12	6.04	16.08	0.17	5.21	2572	67.3	1.543	84.7
5	57.40	9.72	5.02	16.68	0.14	5.46	2581	68.6	1.545	85.2
6	57.64	10.32	4.00	17.28	0.11	5.71	2589	69.9	1.546	85.7
7	60.65	7.29	7.44	12.71	0.18	5.92	2559	66.7	1.536	81.5
8	60.89	7.89	6.42	13.31	0.15	6.17	2571	68.1	1.539	82.0
9	61.13	8.49	5.40	13.91	0.12	6.42	2583	69.4	1.541	82.5
10	61.37	9.09	4.38	14.51	0.09	6.67	2595	70.7	1.543	83.0

value of the refractive index (at the crystal level) will give the coatings a high shine.

In the phase diagram of the ternary system CaO–B_2O_3–SiO_2 the experimental compositions lie in the region of stable liquation. If it is observed in a multicomponent oxide system, liquation can manifest as an opacifier of the glass coating and as a factor imparting good spreadability to the glaze.

The spreadability factor $K_s = D_{fire}/D_{ini}$ was determined by heat-treatment of pellets (D_{ini} = 20 mm, h = 5 mm), prepared by tamping powdered bodies, at 950 and 1050°C for 1 h (Fig. 2). At 950°C the products of firing comprise glass ceramic material (fixed crystal phase — devitrite, wollastonite and others); pellet spreadability was not observed.

Firing at 1050°C resulted in melting and dissolution of crystalline phases and formation of glassy coatings with different spreadability, saturated with gas bubbles. The compositions 1, 3 and 6, whose batches contained 10% perlite with the datolite/cullet ratio varying from 2 to 0.8 (see Fig. 1), exhibited the best spreadability. A correlation was established between the spreadability of glazes and the ratio of the oxides B_2O_3 and Al_2O_3 in there chemical makeup. The condition for good spreadability in the oxide system studied here is B_2O_3/Al_2O_3 (see Fig. 2).

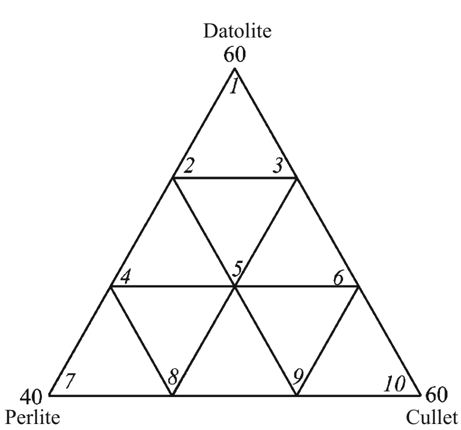


Fig. 1. Material composition of non-frit glazes.

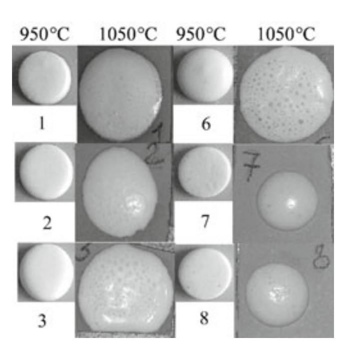
To reduce gas formation and to obtain high-quality coatings it was proposed that datolite and perlite be pre-fired at 800°C, which studies have shown to promote the removal of chemically bound water (water of crystallization and constitution) contained in them.

Considering the significant effect of the slip dispersity on glass formation, the melting temperature and coating quality subsequent studies were performed on two types of slips: *1*) slip with normal dispersity, obtained by mixing the raw materials with themselves and with water after sieving through a No. 0071 sieve; *2*) ultradisperse slip obtained by wet milling in a planetary mill.

Wet milling of slip with composition *1* in a planetary mill gave the solid phase ultradispersity: > 80% of the particles were smaller than 5 μm, while the average size of the particles in slip prepared by the conventional technology is 40 – 60 μm (Fig. 3).

It should be noted that together with intense comminution centrifugal planetary mills, being the most energy consuming, act on the physical-chemical state and structure of a material, i.e., they activate the material chemically and mechanically.

Prepared slips (W_{rel} = 46 – 50%) were poured and brushed on a fired ceramic sample. Next, the samples were



Composition	$K_s = \dfrac{D_{1050°C}}{D_{ini}}$	$\dfrac{B_2O_3}{Al_2O_3}$
1	1.712	3.94
2	1.325	2.36
3	1.587	3.19
6	1.575	2.58
7	1.000	0.98
8	1.050	1.23

Fig. 2. Exterior view of the products of heat-treatment and the ratio B_2O_3/Al_2O_3 as the spreadability factor K_s of non-frit glazes.

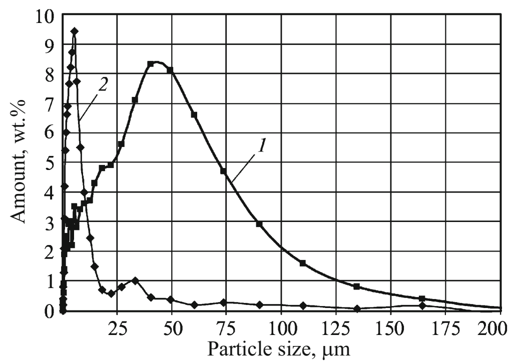


Fig. 3. Differential particle-size distribution curves for slips *1* and *2* of raw glazes (Microsizer 201S).

dried and fired in a muffle furnace at temperatures 950, 1000, 1050 and 1100°C with soaking for 0.5 h at these temperatures.

Transparent gloss coatings were obtained from the ultradisperse slip *2* even at 950°C. Firing at 1000°C improved coating spreadability, increased shine (64 – 66%) and decreased the number of pin holes. The coatings were light beige with no crackling or chipping. The coatings obtained from slip *1* at 950 and 1000°C were sintered with a rough matte surface and they started to vitrify at 1050°C and acquired surface smoothness and shine at 1100°C. Thus, a consequence of ultradispersity and mechanical activation of the slip *2* was a decrease of the firing temperature of the glaze by at least 100°C.

The following technological parameters were formulated for the low-melting non-frit glazes obtained in the system datolite–perlite – cullet from the results of this work:

– the ratio B_2O_3/Al_2O_3 in the chemical makeup of the glaze must be greater than 2.5, for which more than 10% perlite must be introduced into the slip;

– datolite and perlite must be pre-fired at 800°C in order to remove the chemically bound water and decrease the gas release during coating formation;

– the slip must be formed by wet-milling in high-efficiency mills in order to obtain ultradispersity (particle size ≤ 5 μm) and mechanical-chemical activation.

If these recommendations are followed, then it will be possible to obtain high-quality coatings with firing temperature 950 – 1000°C. The new transparent non-frit glazes can be used in the production of artistic ceramics and, with coloring and opacification with ceramic pigments, in the production of ceramic articles for construction, successfully competing with frit glazes because of the simplicity of the technological process and the low cost.

REFERENCES

1. A. P. Zubekhin, N. V. Tabarina, N. D. Yatsenko, and V. P. Rat'kova, "A resource-saving technology for obtaining facing tile," *Steklo Keram.*, No. 6, 3 – 5 (1996); A. P. Zubekhin, N. V. Tabarina, N. D. Yatsenko, and V. P. Rat'kova, "A resource-saving technology for fabricating tile," *Glass Ceram.*, **53**(6), 161 – 163 (1996).
2. A. M. Salakhov, O. V. Spirina, V. I. Remiznikova, and V. G. Khozin, "Low-melting glaze for construction ceramics," *Steklo Keram.*, No. 5, 19 – 20 (2001); A. M. Salakhov, O. V. Spirina, V. I. Remiznikova and V. G. Khozin, "Low-melting glaze for structural ceramics," *Glass Ceram.*, **58**(5 – 6), 174 – 175 (2001).
3. A. G. Tkachev, O. N. Tkacheva, and I. S. Solov'eva, "Production of low-melting glazes without frit melting," *Steklo Keram.*, No. 11, 378 — 379 (2002); A. G. Tkachev, O. N. Tkacheva, and I. S. Solov'eva, "Production of low-melting Ggazes without frit melting," *Glass Ceram.*, **59**(11 – 12), 378 — 379 (2002).
4. N. N. Ermolenko, "Chemical structure and some properties of oxide glasses," in: *Physical-Chemical Principles and Scientific-Technological Progress in the Technology of Glass and Glass Crystal Materials Using Secondary Raw Materials* [in Russian], MISI – BTISM, Moscow (1987), pp. 77 – 88.
5. A. A. Appen, *Chemistry of Glass* [in Russian], Khimiya, Leningrad (1974).